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**MANUFACTURING METHOD OF LITHIUM
SECONDARY BATTERY AND POSITIVE
ELECTRODE ACTIVE MATERIAL FOR LITHIUM
SECONDARY BATTERY**

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[Problems to be Solved by the Invention]

The;al -LIALO manufacturing method and the;al of anode material and its anode material where content of (2) is high -LIALO lithium secondary battery which uses anode material where content of (2) is high is offered.

[Means to Solve the Problems]

1. 7 and 0 $\Leftarrow Y \Leftarrow$ in 0.5 ranges, element M is metal element of the one kind or more which can become ion of trivalent .) Possessing, you adopt lithium secondary battery 1 which designates that it becomes asfeature. XAs for X and Y which show composition ratio 0 Possessing positive electrode 2 and include negative electrode active material negative electrode 3 and nonaqueous electrolyte which include positive electrode active material , Li (X) Al which becomes, as theaforementioned positive electrode active material the;al -LIALO includes (2) crystal (1 -Y) M (Y) O the composition which becomes (2)

[Selected Drawing]

Figure 1

1:リチウム二次電池
2:正極電極
3:負極電極
4:セパレータ

[Claim(s)]

[Claim 1]

1. 7 and $0 \leq Y \leq 0.5$ ranges, element M is element of the one kind or more which can become ion of trivalent .)

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Possessing, lithium secondary battery . which designates that it becomes as **feature** XAs for X and Y which show composition ratio 0 Possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , lixa 11 which becomes, as theaforementioned positive electrode active material the;al -LIALO includes 2 crystal -ymy composition which becomes O2

[Claim 2]

1. 3 and $0 \leq W \leq 0.5$ ranges, element L is element of the one kind or more which can become ion of trivalent .).

Possessing, lithium secondary battery . which designates that it becomes as **feature** VAs for v and W composition ratio is shown 0 Possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , livia 11 which becomes, as theaforementioned positive electrode active material the;ga -LIALO includes 2 crystal -wlw composition which becomes O2

[Claim 3]

Possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , it becomes, The;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) composition and the;ga which become O (2) -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) possessing composition which becomes O (2) as aforementioned positive electrode active material , lithium secondary battery . which designates that it becomes as **feature**

1. 7 and $0 \leq Y \leq 0.5$ ranges, element M and element L are element of one kind or more which can become ion of respective trivalent . X 1. 3 and $0 \leq W \leq 0.5$ and 0 V However, as for v, W, X and Y which show composition ratio , 0

[Claim 4]

Aforementioned;al -LIAL lixa 11 which includes O2 crystal -ymy lithium secondary battery . which is stated in any of Claim 1 or Claim 3 which designates that average particle diameter of powder of composition which becomes the O2 is 20;mu m or less as **feature**

[Claim 5]

Aforementioned;ga -LIAL livia 11 which includes O2 crystal -wlw lithium secondary battery . which is stated in any of Claim 2 through Claim 4 which designates that average particle diameter of powder of composition which becomes the O2 is 20;mu m or less as **feature**

[Claim 6]

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As carbon powder is contained as aforementioned negative electrode , as theaforementioned negative electrode active material metallic lithium being installed in surface , it canhave those which become, lithium secondary battery . which is stated in any of the Claim 1 through Claim 5 which designates that initial discharge is done after battery assembly andbecomes as feature

[Claim 7]

As it mixes aluminum alkoxide and lithium compound in addition to organic solvent ,vis-a-vis aforementioned aluminum alkoxide 1mole reacting including water of 3 mole or more , removing aforementioned organic solvent and aforementioned waterafter reaction termination , in making dried matter , said dried matter with temperature of 200*or higher 600* or below 2 hours or more calcining depending, The;al -LIAL manufacturing method . of positive electrode active material for lithium secondary battery which designates that positive electrode active material which consists of composition which includes O2 crystal is obtained as feature

[Claim 8]

By fact that 550 * exceeding, 2 hours or more it heats aforementioned dried matter with temperature of 600 *or below , the;al -LIAL O2 crystal andthe;ga -LIAL manufacturing method . of positive electrode active material for lithium secondary battery which is stated in Claim 7 which designates that positive electrode active material which consists of composition which includes O2 crystal is obtained as feature

[Claim 9]

manufacturing method . of positive electrode active material for lithium secondary battery which is stated in Claim 7 or Claim 8 which designates that it mixes in addition with to aforementioned aluminum alkoxide and aforementioned lithium compound , alkoxide of metal of the any one kind or more of V, Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi in addition to aforementioned solvent as feature

[Description of the Invention]

[0001]

[Technological Field of Invention]

this invention, being a anode material and its manufacturing method for lithium secondary battery and somethingregarding lithium secondary battery , especially, is something regarding manufacturing method of composition which includes lithium secondary battery and Lialo (2) crystal whichdesignate composition which includes Lialo (2) crystal as positive electrode active material .

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[0002]

[Prior Art]

Among lithium secondary battery, as for battery which is called lithium ion secondary battery, lithium ion making use of positive electrode active material and negative electrode active material which intercalation-deintercalation it is a battery where charge-discharge is done by fact that coming and going it does the lithium ion between positive electrode and negative electrode it is possible.

When here, desirable condition is listed as positive electrode active material of lithium secondary battery, it has possessed crystal structure which has acceptable site, lithium ion scattering can do (1) many lithium ion easily inside (2) crystal structure, (3) positive electrode active material itself the toxicity to be little is inexpensive as much as possible with chemically stable, synthesis of (4) active substance is easy, or other condition can be illustrated.

[0003]

Presently, Li CoO (2) (Co system) and Li Mn (2) O (4) (Mn system) etc is used for positive electrode active material of lithium secondary battery.

Li CoO (2) designates halite structure type as basic structure, shows layered structure by fact that crystal is warped a little, lithium ion insertion (intercalate) or removal charge-discharge is done by fact that (deintercalation) vis-a-vis this interlayer.

In addition, Li Mn (2) as for O (4) with spinel structure type, lithium ion of tetrahedron site has participated in charge-discharge.

When these Li CoO (2) and Li Mn (2) producing O (4), are produced by fact that high temperature firing it does these mixed powder as starting material, CoO (3) powder and Li (2) blend of CO (3) powder and Li (2) making use of CO (3) powder and MnO (2) powder and blend etc.

[0004]

But, Li CoO (2), in order to designate Co which is a strategy substance and as main component with expensive, are times when problem occurs in supply of starting material.

In addition Li Mn (2) O (4), with 50 % or higher Mn melting in electrolyte solution, is a problem that causes decrease of battery performance.

TRANSLATION STALLED electronic equipment secondary battery capacity increase electrode active substance capacity increase cycle lifetime, output characteristic property improvement cost reduction

[0005]

By way, the γ-LiAlO as for (2), as constituent material of

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electrolyte holder of molten carbonate fuel cell it is known generally that it uses, but these;ga-LIALO (2) and the;al-LIALO report which uses (2) as positive electrode active material of the lithium secondary battery has not done at present.

Substituting portion of Co which is included in Li CoO (2) in Al, example which uses composition which it acquires as active substance is shown in below-mentioned patent literature 1.

When Li CoO (2) with the;al which possesses same crystal structure -LIALO(2) is included in active substance, it is disclosed in this patent literature 1, but when composition ratio of Al exceeds 0.1, when battery capacity decreases, from fact that statement has done, With this patent literature 1 extremely little;al-LIALO example which with Li CoO (2) uses (2) only is disclosed.

[0006]

By way, in below-mentioned patent literature 1, the;al-LIALO with lialo(2) synthesizing (2) the;al-lialo, it has originated in not being able to synthesize (2) with alone.

Namely, it can use to production of Lialo (2) solid phase sintering method and the sol-gel method, but when it calcined according to place where inventor of this application experiences concerning solid phase sintering method, making use of lithium carbonate and the aluminum hydroxide, the;ga-lialo synthesis of (2) was possible, but the;al-lialo (2) synthesis is difficult, The;al-LIALO not be able to acquire single phase of (2), the;al-type + the;be-type or the;al-type + the;be-type + the;ga-type those of mixed phase structure only are acquired.

In addition, although the;al-LIALO X-ray diffraction data of (2) it is disclosed public in database (No of ASTM card . 74 - 2232), as for this data there is a status where actual measurement data is not acquired with synthetic product to be no more than to last a calculated value.

[0007]

On one hand, in order for there to be a below-mentioned patent literature 2 concerning sol-gel method, report is already done, but as for this in report to last the;ga-LIALO concerning manufacturing method of (2), description the;al-LIALO concerning (2) is not completely done.

[0008]

[Patent Literature 1]

Japan Unexamined Patent Publication Hei 11- 7958 disclosure

[Patent Literature 2]

Japan Patent Application Sho 60- 135720 disclosure

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[0009]

[Problems to be Solved by the Invention]

Like above, the;al -type , lialo (2) crystal synthesis being difficult to until recently, because the;al -type single phase thing is not acquired, composition to which the;al -type includes lialo (2) crystal concerning applicable whether or not as positive electrode active material for lithium secondary battery was unclear completely.

these inventors this ;al -LIALO invented synthetic method of composition which includes (2) crystal mainly in novel , the;al which is synthesized-LIALO when composition which includes (2) crystal is applied to the positive electrode active material of lithium secondary battery , discovered fact that charge-discharge capacity which is superior is shown, arrived in this invention .

In addition, these inventors when it applies to positive electrode active material the;ga -LIALO concerning (2) crystal , discovered fact that charge-discharge capacity which is superior in comparison with conventional Li CoO (2) crystal is shown, arrived in this invention .

As for this invention considering to above-mentioned situation , being something which it is possible, the;al -LIALO (2) or the;ga -LIALO the manufacturing method and the;al of anode material and its anode material where content of (2) is high -LIALO (2) or the;ga -LIALO it designates that lithium secondary battery which uses anode material where content of (2) is high is offered as the objective .

[0010]

[Means to Solve the Problems]

In order to achieve above-mentioned objective , this invention adopted the configuration below.

1. 7 and $0 \leq Y \leq 0.5$ ranges, element M is element of the one kind or more which can become ion of trivalent .)

Possessing, it designates that it becomes as feature.

Furthermore;al -LIALO as for (2) crystal , space group R- 3 m and No. It is a crystal which is displayed with 166. XAs for X and Y which show composition ratio 0Li (X) Al where lithium secondary battery of this invention becomes, possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material , as aforementioned positive electrode active material the;al -LIALO includes (2) crystal (1 -Y) M (Y) O composition which becomes (2)

[0011]

1. 3 and $0 \leq W \leq 0.5$ ranges, element L is element of the one kind or more which can become ion of trivalent .)

Possessing, it designates that it becomes as feature.

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Furthermore, the γ -LiAlO₂ as for (2) crystal, space group P4 (1) 2 (1) 2, No. It is a crystal which is displayed with 92. VAs for v and W composition ratio is shown 0. In addition, Li (V) Al where lithium secondary battery of this invention becomes, possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material, as aforementioned positive electrode active material the γ -LiAlO₂ includes (2) crystal (1 - W) L (W) O composition which becomes (2)

[0012]

In addition, lithium secondary battery of this invention becomes possessing positive electrode and include negative electrode active material negative electrode and nonaqueous electrolyte which include positive electrode active material, The γ -LiAlO₂ Li (X) Al which includes (2) crystal (1 - Y) M (Y) composition and the γ -LiAlO₂ which become O (2) -LiAlO₂ Li (V) Al which includes (2) crystal (1 - W) L (W) possessing composition which becomes O (2) as aforementioned positive electrode active material, it designates that it becomes as feature.

1. 7 and $0 \leq Y \leq 0.5$ ranges, element M and element L are element of one kind or more which can become ion of respective trivalent. X 1. 3 and $0 \leq W \leq 0.5$ and 0 V. However, as for v , W , X and Y which show composition ratio, 0

[0013]

As for above-mentioned lithium secondary battery, the γ -type or being something which uses composition to which the γ -type includes LiAlO₂ (2) crystal of any one or both as positive electrode active material, as for this composition atomic weight of the per mole to be small in comparison with lithium composite oxide of conventional Co type or Mn type, at same time electrochemical equivalent of lithium equality to conventional lithium composite oxide above that, Because of that it is something where energy density per weight is high.

It is possible to raise energy density by fact that this composition is used for lithium secondary battery.

Especially, the γ -LiAlO₂ as for lithium secondary battery which designates composition which includes (2) crystal as positive electrode active material, initial discharge capacity much high discharge capacity is acquired in comparison with 470 mAh/g and conventional Li CoO (2).

In addition, the γ -LiAlO₂ as for lithium secondary battery which designates composition which includes (2) crystal as positive electrode active material, although initial discharge capacity 300 mAh/g and does not reach in the γ -type, high discharge capacity is acquired in the satisfactory in comparison with conventional Li CoO (2).

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In addition, the;al -type and as for lithium secondary battery which designates the composition to which the;ga -type includes lialo (2) crystal as positive electrode active material, initial discharge capacity becomes 380 mAh/g, the;al -type, the;ga -type discharge capacity of extent of intermediate is almost acquired.

In case of this, high discharge capacity is acquired in satisfactory incomparison with conventional Li CoO (2).

[0014]

1.7 Range is good. If it is a range which drives, the;al -type or the;ga -type can raise stability of crystal structure of lialo (2) crystal, it is possible to insert lithium ion and removal smoothly. Raising from stability of joining structure, in order charge-discharge cycle property to improve, when $0.5 \leq v \leq 1.25$, $0.5 \leq X \leq 1.3$ it puts range of v and X respectively in 1.66 ranges, it is good. X 1.3 0V In addition, composition ratio v of lithium (Li) in above-mentioned composition, X respectively 0

[0015]

In addition, when portion of Al in Lialo (2) crystal is substituted in element m or element l, it is possible furthermore to raise stability of crystal structure of Lialo (2) crystal, from charge-discharge cycle property improves.

Here, element M and element L, with element of any one kind or more of V, the Cr, Mn, Co, Ni, Ga, Y, In, La, Nd, Gd, Yb and Bi, are metal element which can become ion of respective trivalent.

These element M, composition ratio w of L, as for Y exceeding 0, range of 0.5 or less is desirable.

W, when Y exceeds 0.5, because charge-discharge capacity per weight decreases, it is not desirable.

[0016]

In addition, lithium secondary battery of this invention, with lithium secondary battery which is stated first, aforementioned;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) designates that average particle diameter of powder of the composition which becomes O (2) is 20;μm or less as feature.

In addition lithium secondary battery of this invention, with lithium secondary battery which is stated first, aforementioned;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) designates that average particle diameter of powder of the composition which becomes O (2) is 20;μm or less as feature.

[0017]

It is possible to raise charge-discharge capacity, according to

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The;al -LIALO (2) crystal can be synthesized.

Especially, the;al which synthesis makes difficult from until recently by designating sintering temperature as 200 * or higher 550 * or below , -LIALO composition which includes only (2) crystal can be acquired.

[0022]

In addition manufacturing method of positive electrode active material for lithium secondary battery of this invention , with manufacturing method of positive electrode active material for lithium secondary battery which is stated first, by the fact that 550 * exceeding, 2 hours or more it heats aforementioned dried matter with temperature of 600 * or below , the;al -LIALO (2) crystal and the;ga-LIALO designates that positive electrode active material which contains (2) crystal is obtained as feature.

[0023]

According to manufacturing method of positive electrode active material for this lithium secondary battery , by fact that 550 * exceeding, it heats aforementioned dried matter with temperature of 600 * or below , the;al -type and composition to which the;ga -type includes lialo (2) crystal of both simultaneously is acquired.

[0024]

In addition manufacturing method of positive electrode active material for lithium secondary battery of this invention with the manufacturing method of positive electrode active material for lithium secondary battery which is stated first, designates that it mixes in addition to with aforementioned aluminum alkoxide and the aforementioned lithium compound , alkoxide of metal of any one kind or more of V, the Cr , Mn , Co , Ni , Ga , Y, In , la, ND, Gd, Yb and Bi in addition to aforementioned solvent as feature.

[0025]

According to manufacturing method of positive electrode active material for this lithium secondary battery , because the above-mentioned metal alkoxide is added to other than aluminum alkoxide and the aforementioned lithium compound , it is possible to substitute portion of the Al of Lialo (2) crystal in above-mentioned metal , positive electrode active material where stability of crystal structure of Lialo (2) crystal improves, is superior in charge-discharge cycle property can be acquired.

Namely, sintering temperature to be acquired 200 - 550 * in range, the;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) powder of composition which becomes O (2), sintering temperature 550 - 600 * in range, In range where the;al -LIALO Li (X) Al which includes the (2) crystal (1 -Y) M (Y) blend of composition which becomes O (2) and the;ga-LIALO Li (V) Al which includes (2) crystal (1 -W) L

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(W) the composition which becomes O (2) is acquired, sintering temperature 600 * exceeds, The;ga-LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) composition which becomes O (2) is acquired.

1. 7 and $0 \leq Y \leq 0.5$ ranges, element M and element L are element of one kind or more which can become ion of respective trivalent . X1. 3 and $0 \leq W \leq 0.5$ and 0 VFurthermore v, W, X and Y which show composition ratio in theabove-mentioned each composition formula respectively 0

[0026]

[Embodiment of the Invention]

Below, referring to drawing , you explain embodiment of this invention .

one example of lithium secondary battery which is a embodiment of this invention is shown in the Figure 1 .

this lithium secondary battery 1 being something which is called so-called angular type , configuration is done positive electrode of plural (electrode) 2... with, with negative electrode 3* and positive electrode 2 of plural and separator 4* and nonaqueous electrolyte (nonaqueous electrolyte) which are respectivelyarranged between negative electrode 3 as main component .

positive electrode 2* , negative electrode 3* and separator 4* and nonaqueous electrolyte are stored up in battery case 5 whichconsists of stainless steel etc.

And sealing plate 6 is installed in upper part of battery case 5.

safety valve 9 which prevents internal pressure rise of battery is provided almost in center of this sealing plate 6.

It can use to separator 4, nonwoven fabric etc which consists of polyethylene , polypropylene or other porosity polymeric material film , glass fiber , various polymer fiber .

[0027]

positive electrode tab 12* is formed by one end of positive electrode 2* , positive electrode tab 12 a... the said positive electrode tab 12 a... positive electrode lead 12 b which hitch is done is installed in the upper part .

positive electrode terminal 7 which penetrates sealing plate 6 is installed in this positive electrode lead 12 b.

In same way, negative electrode tab 13 a... is formed in one end of negative electrode 3* ,negative electrode tab 13 a... said negative electrode tab 13 a... negative electrode lead 13 b which hitch is done isinstalled in upper part .

negative electrode terminal 8 which penetrates sealing plate 6 is installed in this negative electrode lead 13 b.

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Due to above-mentioned configuration, it is designed in such a way that it can remove current from positive electrode terminal 7 and negative electrode terminal 8.

[0028]

As shown next in Figure 2, negative electrode 3, on negative electrode collector 3 a and this negative electrode collector 3 a which consist of Cu foil etc configuration is done from negative electrode film 3 b which film formation is done.

Aforementioned negative electrode tab 13 a protruding doing in one end of negative electrode collector 3 a, it is formed.

negative electrode film 3 b is formed, for example graphite or other negative electrode active material powder and polyvinylidene fluoride or other binder being mixed.

Furthermore when carbon black or other conduction aid powder is added to negative electrode membrane 3 b, it is.

[0029]

As negative electrode active material, pyrolysate or other various carbon material of coke, amorphous carbon, graphitized carbon fiber, various polymeric material can be used for other than graphite.

In addition to other than carbon material, is possible also fact that metallic lithium, lithium and various metal oxide etc which are represented in alloy, tin of various metal are used.

metallic lithium and alloy are good even with those of foil not just powder always.

In addition, poly tetrafluoroethylene, polyimide etc can be used for other than polyvinylidene fluoride, as binder of negative electrode 3.

[0030]

Furthermore, when above-mentioned various carbon material are used as the negative electrode active material, you can use attachment metallic lithium in surface of negative electrode film 3 b which consists of these carbon material as negative electrode.

metallic lithium which is used here be able to use things such as powder and thin band or other various shape, these should have been pasted together in surface of negative electrode film 3 b.

[0031]

positive electrode 2, positive electrode collector which consists of for example Al foil etc (current collector) to 2 A and on positive electrode collector 2 a positive electrode film which film formation is done (electrode film) configuration is done from 2 B.

Aforementioned positive electrode tab 12 a protruding doing in

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one end of positive electrode collector 2 a, it is formed.

As for positive electrode membrane 2 b, solid component and binder being mixed, being something which formed in film, at least positive electrode active material powder (electrode active substance) and the conduction aid powder is included in solid component.

[0032]

As and shown in Figure 2, positive electrode film 2 b and negative electrode film 3 b through the separator 4, it is opposed.

Furthermore, in order to make explanation simple regarding Figure 2, each current collector 2 a, each electrode film 2 b, shape which 3 B film formation is done has been shown in one surface of 3 A, but each electrode film 2 b, 3 B each current collector 2 a, the fact that film formation it is possible to do is of course in both surfaces of 3 A.

[0033]

In addition, the;al -lialo Li (X) Al which includes (2) crystal (1 -Y) M (Y) powder of composition which becomes O (2) can be used as positive electrode active material which is included in positive electrode membrane 2 b.

In addition the;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) it is possible also as positive electrode active material, to use powder of composition which becomes O (2).

Furthermore, the;al -LIALO Li (X) Al which includes (2) crystal (1 -Y) M (Y) blend of powder of composition which becomes O (2) and the;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) powder of composition which becomes O (2) can be used as positive electrode active material.

Here,;al -LIALO as for (2) crystal, space group R-3 m and No. With crystal which is displayed with 166, in addition the;ga -LIALO as for (2) crystal, space group P4 (1) 2 (1) 2, No. It is a crystal which is displayed with 92.

1. 7 and $0 \leq Y \leq 0.5$ ranges, element M and element L are element of one kind or more which can become ion of respective trivalent. X 1. 3 and $0 \leq W \leq 0.5$ and 0 VV, W, X and Y which show composition ratio in above-mentioned each composition formula respectively 0

[0034]

As for lithium secondary battery of this embodiment, the;al -type or being something which uses composition to which the;ga -type includes lialo (2) crystal of any one or both as positive electrode active material, as for this composition atomic weight of per mole to be small in comparison with lithium composite oxide of conventional Co type or Mn type, at the same time electrochemical equivalent of lithium equality to conventional lithium composite oxide above that, It is

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something where energy density per weight is high.

By fact that this composition is used for positive electrode active material, it is possible to raise energy density of lithium secondary battery.

Especially, it is something whose it is possible the;al -LIALO (2) crystal Li CoO (2) with to have had similar layer halite structure, to insert the lithium ion and removal easily.

Because of this, the;al -LIALO by fact that it uses composition which includes (2) crystal as positive electrode active material, much high discharge capacity can be acquired in comparison with conventional Li CoO (2).

In addition, the;ga -LIALO as for composition which includes (2) crystal, although charge-discharge capacity does not reach in the;al -type, high discharge capacity is acquired in satisfactory in comparison with Li CoO (2).

In addition the;ga -LIALO composition which includes (2) crystal can acquire cycle property which is superior in comparison with the;al -type.

Furthermore, the;al -type and as for composition to which the;ga -type includes lialo (2) crystal, the;al -type, the;ga -type discharge capacity of extent of intermediate is almost acquired.

In case of this, high discharge capacity is acquired in satisfactory in comparison with conventional Li CoO (2).

[0035]

1.7 Range is good. If it is a range which drives, the;al -type or the;ga -type can raise stability of crystal structure of lialo (2) crystal, it is possible to insert lithium ion and removal smoothly. Raising from stability of joining structure, in order charge-discharge cycle property to improve, when $0.5 \leq v \leq 1.25$ $0.5 \leq X \leq$ it puts range of v and X respectively in 1.66 ranges, it is good. X 1.3 0V composition ratio v of lithium (Li) in above-mentioned composition, X respectively 0

[0036]

When composition ratio v and X are 0 respectively, to become state where lithium is not completely included in positive electrode active material, because it does not function as lithium secondary battery it is not desirable.

In addition, composition ratio v being 1.3 or greater, when composition ratio x is 1.7 or greater, because the;al -type, the;ga -type synthesis of lialo (2) crystal becomes difficult, it is not desirable.

[0037]

In addition, when the;al -type and the;ga -type portion of Al in lialo (2) crystal is substituted in element m and element l, it is possible furthermore to raise stability of crystal structure of lialo (2) crystal, from charge-discharge cycle property

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improves.

Here, element M and element L, with element of any one kind or more of V, the Cr, Mn, Co, Ni, Ga, Y, In, Ia, ND, Gd, Yb and Bi, are element which can become ion of respective trivalent.

When you think from viewpoint of energy density, those where atomic weight is small as substitute element are good.

These element M, composition ratio w of L, as for Y exceeding 0, range of 0.5 or less is desirable.

When composition ratio w and Y respectively exceed 0.5, because charge-discharge capacity per composition weight decreases, it is not desirable.

[0038]

In addition, the;al-LIALO Li (X) Al which includes (2) crystal (1-Y) M (Y) as for average particle diameter of powder of composition which becomes O (2) it is desirable to be 20;μm or less.

In same way, the;ga-LIALO Li (V) Al which includes the(2) crystal (1-W) L (W) it is desirable also for average particle diameter of powder of composition which becomes O (2) to be 20;μm or less.

By fact that average particle diameter of powder of each composition is designated as 20;μm or less, it is possible to raise from charge-discharge capacity.

[0039]

In addition, as positive electrode active material, the;al-LIALO Li (X) Al which includes (2) crystal (1-Y) M (Y) case where blend of powder of composition which becomes O (2) and the;ga-LIALO Li (V) Al which includes (2) crystal (1-W) L (W) powder of composition which becomes O (2) is used, When charge-discharge cycle property is seriously considered, when it makes many, the;ga-type content in comparison with the;al-type, when charge-discharge capacity is seriously considered, it makes many the;al-type content in comparison with the;ga-type it is good.

Especially, if even with when charge-discharge capacity is seriously considered, the;al-LIALO the;ga of trace-LIALO it tries to include (2) crystal in (2) crystal, cycle property it can improve.

In case of this, the;ga in positive electrode active material it is good for -type to designate blend ratio as 20 mass % or greater.

[0040]

In addition, it is good adding polyaniline, polypyrrole, polythiophene, polyimidazole or other conductive polymer material to above-mentioned positive electrode active

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material, when especially polyaniline is added, it is good.

As for these conductive polymer material because in electrochemically stability, furthermore it is superior in electronic conductivity, resistance of positive electrode film 2 b is decreased by the fact that conductive polymer material is added, internal impedance of battery decreases and there is an effect to which charge-discharge capacity improves.

As for composition ratio of polyaniline or other conductive polymer material in positive electrode active material, range of 0.1 mass % or greater 5 mass % or less is desirable.

Because under 0.1 mass % addition effect of conductive polymer material which description above is done you cannot see composition ratio, not to be desirable, when the composition ratio exceeds 5 mass %, because electronic conductivity inhibition is done with the excessive sheath of conductive polymer material, it is not desirable.

[0041]

Next, it is desirable to use carbon black, acetylene black, graphite, carbon fiber or other carbon material, as conduction aid which is included in positive electrode membrane 2 b.

In addition it is desirable to use polyvinylidene fluoride, polytetrafluoroethylene, polyimide or other polymer binder, as binder.

In addition it is desirable to use metal foil, metal mesh, expanded metal etc, as positive electrode collector 2 a, in addition these material Al, Ti and stainless steel etc are desirable.

[0042]

As for composition ratio of positive electrode membrane 2 b, positive electrode active material 60 - 90 weight%, conduction aid 5 - 20 mass %, binder range of 5 - 20 mass % are desirable.

[0043]

Those which melt one, two or more kinds of solute which consists of CF₃SO₂(2) N or other lithium salt can be used. Next in mixed solvent which mixes for example ethylene carbonate, butylene carbonate or other cyclic carbonate ester and dimethyl carbonate, methylethyl carbonate, diethyl carbonate or other linear carbonate ester nonaqueous electrolyte (nonaqueous electrolyte) as, Lipf (6), Libf (4), Liasf (6), Liclo (4), Licf (3) So(3), Li

[0044]

In addition, replacing to above-mentioned nonaqueous electrolyte, it is possible also to use solid electrolyte (nonaqueous electrolyte).

As solid electrolyte, polyethylene oxide or other lithium ion conduction polymer which contains above-mentioned solute

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and impregnating above-mentioned nonaqueous electrolyte in polyethylene oxide, polyvinylidene fluoride, polyacrylonitrile or other polymer matrix, gel electrolyte etc which becomes you can use.

[0045]

lithium secondary battery 1 of this embodiment is produced, first, it mixes powder of the positive electrode active material with carbon black or other conduction aid, this blend, it adds to NMP or other dispersion medium where beforehand polyvinylidene fluoride or other binder and polyaniline are melted and makes slurry, this slurry the application after doing, adding heat removal it does dispersion medium in positive electrode collector with doctor blade method, etc it produces positive electrode 2 by compressing with the press etc.

Next, it mixes powder of negative electrode active material with according to need carbon black or other conduction aid, this blend, it adds to NMP or other dispersion medium where polyvinylidene fluoride or other binder is melted beforehand and makes the slurry, this slurry application after doing, adding heat removal it does the dispersion medium in negative electrode collector with doctor blade method, etc it produces negative electrode 3 by compressing with press etc.

[0046]

And, sequential laminating positive electrode 2 and separator 4 and negative electrode 3, it inserts in battery case 5, pouring liquid does nonaqueous electrolyte next, next connects the sealing plate 6 to battery case 5.

lithium secondary battery of this embodiment is acquired this way.

[0047]

In addition, metallic lithium being installed in surface of negative electrode 3, case lithium secondary battery which becomes is produced, positive electrode 2 and separator 4 and the metallic lithium equipped negative electrode sequential laminating, it inserts in battery case 5, pouring liquid does nonaqueous electrolyte next, next connects sealing plate 6 to battery case 5.

After that, it moves to positive electrode 2 by doing initial discharge, with metallic lithium of negative electrode 3 surface as state of lithium ion.

lithium ion which reaches to positive electrode 2 the; α -type or the; γ -type is inserted into lialo (2) crystal.

With this initial discharge, $\text{Li (X) Al (1 - Y) M (Y) O (2)}$ or $\text{Li (V) Al (1 - W) L (W)}$ composition ratio v of Li which is displayed with composition formula of O (2) , value of X improves.

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this way, it is possible to insert in composition which by fact that initial discharge it does metallic lithium which is installed in negative electrode 3 includes LiAlO₂ crystal. lithium content of this said composition improves because of this, it is possible to raise charge-discharge capacity.

Therefore, when metallic lithium is installed in negative electrode 3, lithium content of the positive electrode active material beforehand it should have decreased.

As for composition which includes LiAlO₂ crystal where lithium content is little it is possible, productivity of lithium secondary battery can improve to make the synthesis time relatively short.

Furthermore in order Li_xAl_{1-y}M_yO₂ or Li_xAl_{1-w}L_w composition ratio x of Li which is displayed with the composition formula of O₂, for value of x respectively to become 1.7 and 1.3, when it is synthesized in initial stage, it is not necessary to install Li foil in negative electrode.

[0048]

Next, manufacturing method of positive electrode active material of this embodiment is explained.

First, aluminum alkoxide and lithium compound are prepared as starting material.

As embodiment of aluminum alkoxide, carbon number of aluminum methoxide, aluminum ethoxide, aluminum isopropoxide, aluminum normal propoxide or other alkyl group can use those of 1-10 extent.

In addition lithium chloride, lithium bromide, lithium iodide, lithium fluoride, lithium nitrate, lithium hydroxide, lithium carbonate, lithium citrate etc can be used as lithium compound.

[0049]

Furthermore, when portion of Al_xLi_{1-x}Al which is substituted in metal element M or L_{1-y}M_yO₂ or Li_xAl_{1-w}L_w composition which becomes O₂ is obtained, adding alkoxide of the metal element M or L_x, metal of any one kind or more of Cr, Mn, Co, Ni, Ga, Y, In, La, Nd, Gd, Yb and Bi) as starting material, it is necessary to use.

As alkoxide in this case, carbon number of methoxide, ethoxide, isopropoxide, normal propoxide or other alkyl group can use those of 1-10 extent.

[0050]

Next, throwing these starting material to organic solvent, it mixes.

0054

[0054]

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Next, it calcines 2 hours or more with temperature of 200 * or higher 600* or below vis-a-vis the dried matter of this gel .

The;al -LIALO composition which includes (2) crystal is acquired by calcining.

When sintering temperature is relatively low temperature of 200 * or higher 550* or below , when most all of the;lialo (2) crystal which is included in composition the;al -lialo become the(2) crystal , sintering temperature exceeds 550 * , the;al -lialo the;ga -lialo (2) crystal forms to other than (2) crystal .

When sintering temperature exceeds 600 * , the;al -LIALO (2) crystal is notcompletely formed, the;ga -type single phase composition is acquired.

Furthermore because sintering temperature is formed 200 * at under the;be which islacking in electrochemical activity -LIALO (2) crystal , it is not desirable.

[0055]

In addition if sintering time is 2 hours or more , the;al -type and the;ga -type can calcine necessary and sufficient in formation of lialo (2) crystal .

When sintering time is under 2 hours , because the;be -LIALO (2) crystal isformed, it is not desirable.

In addition, as for sintering time there is not a especially upper limit . When it is an excessive lengthy , because cost of calcining increases,when it makes 96 hours or less, it is good.

In addition as for atmosphere of calcining, it is desirable to do in atmosphere .

Because composition which it acquires, being sintered by calcining, ithas become massive, this powder fragment doing with ball mill or other mill , average particle diameter makes powder of 20; μ m or less .

[0056]

Like above, by fact that sintering temperature is designated as 200 * or higher 550* or below ,the;al -LIALO Li (X) Al which includes only (2) crystal (1 -Y) M(Y) composition which becomes O (2) is acquired.

In addition, by fact that 550 * exceeding, it puts sintering temperature inrange of 600 * or below , the;al -LIALO Li (X) Al which includes(2) crystal (1 -Y) M (Y) blend of composition which becomes O (2) andthe;ga -LIALO Li (V) Al which includes (2) crystal (1 -W) L (W) composition which becomes O (2) is acquired.

Furthermore, when sintering temperature exceeds 600 * , the;ga -LIALO Li (V) Al which includes only (2) crystal (1 -W) L (W) composition which becomesO (2) is acquired.

[0057]

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manufacturing method of positive electrode active material for lithium secondary battery of this embodiment, reacting, designates aluminum alkoxide and lithium compound and water as dried matter of the gel, the;al -LIALO obtains positive electrode active material which contains (2) crystal byfact that it calcines this dried matter, with so-called sol-gel method with manufacturing method, itcan synthesize lialo (2) crystal with calcining relatively low temperature.

Especially, the;al which synthesis makes difficult from until recentlyby designating sintering temperature as 200 * or higher 550* or below, -LIALO composition whichincludes only (2) crystal can be acquired.

In addition, by fact that 550 * exceeding, it heats dried matter of gel with temperature of 600 * or below, the;al -type and it canacquire composition to which the;ga -type includes lialo (2) crystal of both simultaneously.

[0058]

Furthermore, because to of aluminum alkoxide and lithium compound other than element Mor metal alkoxide of element L is added, portion of Al of Lialo(2) crystal element m or it is possible to substitute in element l, the positive electrode active material where stability of crystal structure of Lialo (2) crystal improves, issuperior in charge-discharge cycle property can be acquired.

[0059]

[Working Example(s)]

(Working Example 1)

Throwing to ethanol with mole ratio which shows Lino (3) in the Table 1, it mixed, hydrolysis it did furthermore in order to become the aluminum ethoxide per mole 3mole or more, water to in addition. OC (2) H (6) (3) with lithium nitrate Al aluminum ethoxide

In order that next, water and ethanol are removed from reaction product after hydrolysis, 80 * with 1 week standing doing, it dried.

Next, dried matter of gel after drying powder fragment was done with the agate mortar, milled product after forming with hydrostatic press method, in atmosphere, 200 -1100 * with temperature range 1 - 96 hours was calcined with condition whichis kept.

As shown in Table 1 pyrolysate which it acquires by powder fragment doingwith wet ball mill method, composition of this invention Example 1, 3~18 and Comparative Example 1~6 was acquired.

In Table 1, case where each composition is obtained lithium which isa proportion of starting material (Li) with mole ratio and sintering condition of aluminum (Al) are shown in every

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composition .

[0060]

It measured particle diameter vis-a-vis composition which it acquires.

It did grain size measurement with laser diffraction , particle diameter made median diameter which was sought with laser diffraction .

In addition, produced phase which is included in composition vis-a-vis the composition which is acquired, by X-ray diffraction , identification was done.

measurement result of particle diameter and identification result result of produced phase are shown in Table 1 .

In addition in Figure 3 , X-ray diffraction result of composition (this invention Example 5 , 8, 10, 11) of part is shown.

[0061]

Furthermore, composition of Comparative Example 9 was synthesized those which in order for mole ratio of Li /Al to become with 1.0, mix powder of lithium carbonate and aluminum oxide , 500 * with by 12 hours calcining.

Result of X-ray diffraction of composition which it acquires is shown in the Figure 4 .

Furthermore and, it designated quantity of water as 3 mole vis-a-vis aluminum ethoxide , 500 * with other than thing which 12 hours calcines it synthesized with as similar to this invention Example 1 , 3~18 and Comparative Example 1~6, synthesized composition of Comparative Example 10.

Result of X-ray diffraction of composition which it acquires is shown in the Figure 5 .

[0062]

[Table 1]

[0063]

Li/Al モル比	焼成条件		生成相 (X線回折に よる同定相)	平均粒径 (μm)	初期放電容量 (mAh/g)	
	焼成温度 ($^{\circ}\text{C}$)	保持時間 (時間)				
1.0	150	12	β -LiAlO ₂ α -LiAlO ₂	1以下	50	比較例1
1.0	200	12	α -LiAlO ₂	1以下	200	本発明例1
1.0	500	1	β -LiAlO ₂ α -LiAlO ₂	1以下	50	比較例2
1.0	500	2	α -LiAlO ₂	1以下	—	本発明例3
1.0	500	6	α -LiAlO ₂	1以下	—	本発明例4
1.0	500	12	α -LiAlO ₂	1以下	470	本発明例5
1.0	500	24	α -LiAlO ₂	1以下	—	本発明例6
1.0	550	12	α -LiAlO ₂	1以下	450	本発明例7
1.0	600	12	α -LiAlO ₂ γ -LiAlO ₂	1以下	380	本発明例8
1.0	700	12	γ -LiAlO ₂	1以下	300	本発明例9
1.0	1000	12	γ -LiAlO ₂	1以下	300	本発明例10
1.0	1100	12	γ -LiAlO ₂	1以下	290	本発明例11
1.25	500	12	α -LiAlO ₂	1以下	—	本発明例12
1.25	1000	24	γ -LiAlO ₂	1以下	300	本発明例13
1.3	500	12	α -LiAlO ₂	1以下	—	本発明例14
1.3	1000	24	γ -LiAlO ₂ 不明相	1以下	—	比較例3
1.3	1000	96	γ -LiAlO ₂	1以下	—	本発明例15
1.35	500	12	α -LiAlO ₂	1以下	—	本発明例16
1.35	1000	24	γ -LiAlO ₂ 不明相	1以下	—	比較例4
1.67	500	24	α -LiAlO ₂	1以下	470	本発明例17
1.7	500	24	α -LiAlO ₂ 不明相	1以下	—	比較例5
1.7	500	96	α -LiAlO ₂	1以下	—	本発明例18
1.75	500	96	α -LiAlO ₂ 不明相	1以下	—	比較例6

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[illegible][illegible]

Way it shows in Table 1 , when sintering temperature 150 * with it is low, when(Comparative Example 1) and retention time 1 hour it is short, in (Comparative Example 2) , the be -LIALO (2)had formed.

The;al -LiAlO (2) had formed regardless of mole ratio of Li and Al retention time sintering temperature 200 ° - 550 ° concerning thing(this invention Example 1, 5, 7, 12, 14, 16) of range in 12 hours, in addition, as shown in Table 1 and the Figure 3.

Furthermore, as shown in Table 1 and Figure 3, sintering temperature the;ga-LIALO (2) had formed concerning thing (this invention example 9 and 10, 11, 13 and 15, Comparative Example 3, 4) of 700 ° or higher .

Furthermore concerning Comparative Example 3 and 4 , result of X-ray diffraction , compound the unclear peak which

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identification it is not possible was detected, but these the sintering temperature 1000* are high, because 24 hours and it is long furthermore sintering time this invention example in comparison with 9 and 10 etc, it is thought as the thing which another phase precipitated.

In addition, as shown in Table 1 and Figure 3, sintering temperature the;al-LIALO (2) with the;ga-LIALO both phases of (2) had formed 600 * concerning thing (this invention Example 8).

[0064]

this way, making use of sol-gel method which utilizes aluminum alkoxide, by fact that it calcines 2 hours or more with low temperature of 600 * or below, the;al-LIALO it became clear for composition which contains (2) to be acquired.

Especially, sintering temperature 200 * - 550 * with by fact that it does, the;al-LIALO it became clear for composition which contains only (2) to be acquired.

Furthermore, sintering temperature 600 * with by fact that it does, the;al-type and it became clear for composition where the;ga-type contains lialo (2) of both to be acquired.

[0065]

In addition, as shown in Table 1, the;al-type LIALO composition of (2) single phase as for synthesizable maximum Li / Al mole ratio with (this invention Example 17) under approximately 1.7, the;ga-type LIALO composition of (2) single phase as for synthesizable maximum Li / Al mole ratio is 1.3 or less (this invention example 15).

As Li / Al mole ratio becomes large, it can recognize tendency where sintering time in order to obtain single phase becomes long.

[0066]

In addition, composition of this invention Example 5 and X-ray diffraction result of composition of Comparative Example 9 are shown in Figure 4.

Al (2) diffraction peak of O (3) is detected. Li (2) CO (3) with aluminum oxide As for this invention Example 5 and Comparative Example 9, sintering condition 500 * with 12 hours and is identical condition, but lithium carbonate which is a starting material regarding Comparative Example 9

With this invention Example 5 which on one hand, is synthesized with sol-gel method, the;al-LIALO as for compound other than (2) what it is not detected.

Therefore according to manufacturing method of this invention, composition where the impurity is little can be acquired.

[0067]

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[0068]

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[0069]

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[0070]

[0067]

Furthermore, composition of this invention Example 5 and X-ray diffraction result of composition of Comparative Example 10 are shown in Figure 5.

As for this invention Example 5 and Comparative Example 10, sintering condition 500 ° with 12 hours and is identical condition, but the;al -LIALO the;be -LIALO (2) is formed to other than (2) regarding Comparative Example 10 where addition quantity of water is little.

On one hand, quantity of water is not detected with sufficient this invention Example 5, the;al -LIALO as for compound other than (2) what.

Therefore regarding manufacturing method of this invention, the;be -LIALO there are not times when (2) forms by adding water to fully, they can acquire composition where impurity is little.

[0068]

(Working Example 2)

It designated composition which is synthesized with Working Example 1 as the positive electrode active material, in this it mixed acetylene black at ratio of 10 mass % as conductor, it threw this blend, to N-methyl-pyrrolidone solution which melts polyvinylidene fluoride and made the slurry.

this slurry, with doctor blade method application was done next on aluminum foil of the thickness 20;μm, furthermore N-methyl-pyrrolidone adding heat removal was done.

positive electrode was produced this way.

You inserted in test cell canister with state which repeats separator and metallic lithium foil (negative electrode) which consist of positive electrode and porous polypropylene which it acquires you produced test cell furthermore by pouring liquid doing the nonaqueous electrolyte.

Those which in order to become concentration of 1 mole/liter, melt Liclo (4) were used. In nonaqueous electrolyte, in mixed solvent of ethylene carbonate 50 volume % and diethyl carbonate 50 volume % lithium perchlorate

[0069]

Until first per positive electrode active material (composition) with constant current density of 50 mA/g 4.3 V ago, concerning test cell which it produces, it charged, after that per positive electrode active material with constant current density of 50 mA/g discharged to 3.0 V.

It shows in Table 1 with discharge capacity at time of this as the initial discharge capacity.

[0070]

□0073□

[0073]

Li/Al モル比	焼成条件		生成相	平均粒径 (μm)	初期放電 容量 (mAh/g)	
	焼成温度 ($^{\circ}\text{C}$)	保持時間 (時間)				
1.0	500	12	$\alpha\text{-LiAlO}_2$	1	470	本発明例 5
1.0	500	12	$\alpha\text{-LiAlO}_2$	7	440	本発明例 19
1.0	500	12	$\alpha\text{-LiAlO}_2$	14	350	本発明例 20
1.0	500	12	$\alpha\text{-LiAlO}_2$	23	70	比較例 7
1.0	1000	12	$\gamma\text{-LiAlO}_2$	1	300	本発明例 10
1.0	1000	12	$\gamma\text{-LiAlO}_2$	8	250	本発明例 21
1.0	1000	12	$\gamma\text{-LiAlO}_2$	16	170	本発明例 22
1.0	1000	12	$\gamma\text{-LiAlO}_2$	24	50	比較例 8

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(Working Example 4)

OC (2) H (6) (3) respectively, with aluminum ethoxide and lithium nitrate was thrown in ethanol, other than thing which is made condition which shows sintering condition in Table 3 composition was acquired with assimilar to Working Example 1. Y OC (2) H (6) (3) with yttrium ethoxide Co cobalt ethoxide

test cell was produced concerning composition which it acquires, to similar to above-mentioned Working Example 2, with same condition as Working Example 2 charge-discharge was done to 10 cycle.

And it measured discharge capacity after initial discharge capacity and 10 cycle, measured also degradation ratio of discharge capacity to 10 cycle from initial stage.

Result is shown in Table 3.

To other than sintering condition and discharge result, it showed also composition formula of the composition in Table 3.

Way it shows in Table 3, the;al-type, the;ga-type in case of which being attached, degradation ratio greatly improving you understand by adding Co and Y with Al substitution.

Especially;ga it understands that -type degradation ratio is small.

[0074]

[Table 3]

[0075]

結晶相	組成式	放電容量(mAh/g)		劣化率(%)	備考
		初期	10 サイクル後		
α 型	LiAlO_2	470	350	26	焼成温度 500°C
α 型	$\text{LiAl}_{0.9}\text{Co}_{0.1}\text{O}_2$	450	400	11	保持時間 12 時間
α 型	$\text{LiAl}_{0.9}\text{Y}_{0.1}\text{O}_2$	430	410	5	粒径 1 μm 以下
γ 型	LiAlO_2	300	250	17	焼成温度 1000°C
γ 型	$\text{LiAl}_{0.9}\text{Co}_{0.1}\text{O}_2$	290	270	7	保持時間 12 時間
γ 型	$\text{LiAl}_{0.9}\text{Y}_{0.1}\text{O}_2$	280	280	0	粒径 1 μm 以下

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Throwing graphite as negative electrode active material , to N-methyl-pyrrolidone solution which melts polyvinylidene fluoride ,it made slurry , with doctor blade method application did this slurry on copper foil of thickness 20;mu m , it produced positive electrode furthermore by adding heat removal doing N-methyl-pyrrolidone .

Next, this invention Example 5 in Table 1 (;al -type) and other than thing which uses composition of this invention example 10 (;ga -type) positive electrode was produced with as similar to Working Example 2.

test cell was drawn up and, making use of these negative electrode and positive electrode ,to similar to Working Example 2.

With same condition as Working Example 2 charge-discharge was done to 10 cycle vis-a-vis test cell which it acquires, discharge capacity of 10 cycle later was measured.

As a result, with test cell which uses composition of this invention Example 5 (al-type), the discharge capacity of 10 cycle later showed 300 mAh/g.

In addition concerning test cell which uses composition of this invention example 10 (;ga -type),discharge capacity of 10 cycle later showed 230 mAh/g .

this way, by fact that negative electrode which sticks metallic lithium foil is used, lithium inserting in positive electrode active material, positive electrode active material Li content improves, it understands that high discharge capacity is shown even with when charge-discharge cycle was repeated.

Next, this invention Example 5 in Table 1 (;al -type) and composition of this invention example 10 (;ga -type)

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was mixed, in order for composition ratio of composition of this invention example 10 (ga-type) to become range of 0 - 100 mass %, other than thing which uses positive electrode active material which was adjusted positive electrode was produced with as similar to the Working Example 2.

And, making use of these positive electrode test cell was produced to similar to above-mentioned Working Example 2, with same condition as Working Example 2 charge-discharge was done to 10 cycle.

And discharge capacity after initial discharge capacity and 10 cycle was measured, degradation ratio (cycle degradation rate) of discharge capacity to 10 cycle was sought.

Result is shown in Figure 6.

As shown in Figure 6, when the ga-type content exceeds 20 mass %, cycle degradation rate becomes 20% or lower, it understands that cycle property which is superior is shown.

[0077]

[Effects of the Invention]

As above, explained in detail, as for lithium secondary battery of this invention, the al-type or being something which uses composition to which the ga-type includes lialo (2) crystal of any one or both as positive electrode active material, as for the this composition atomic weight to be small in comparison with lithium composite oxide of conventional Co type or Mn type, at same time electrochemical equivalent of lithium equality to the conventional lithium composite oxide above that, It is something where energy density per weight is high.

It is possible to raise energy density by fact that this composition is used for lithium secondary battery.

[0078]

In addition, portion of Al in Lialo (2) crystal by fact that it substitutes in element m or element l, it is possible, can improve from charge-discharge cycle property furthermore to raise stability of crystal structure of Lialo (2) crystal.

[0079]

In addition as for lithium secondary battery of this invention, carbon powder is included as aforementioned negative electrode active material, at same time can install metallic lithium in surface and it can have negative electrode which becomes, being something where initial discharge is done after battery assembly and becomes, according to this lithium secondary battery, It is possible to insert in composition which by fact that initial charging it does metallic lithium which is installed in negative electrode includes Lialo (2) crystal lithium content of this said composition improves because of this, it is possible to raise charge-discharge capacity.

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3b

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3a

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3

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2b

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2a

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2

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1

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Drawings

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separator

3b

negative electrode film

3a

negative electrode collector

3

negative electrode

2b

positive electrode membrane

2a

positive electrode collector

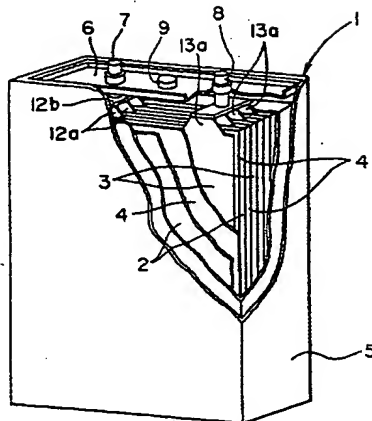
2

positive electrode

1

lithium secondary battery

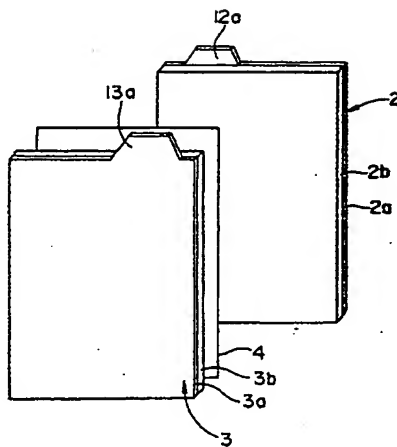
[Figure 1]



1: リチウム二次電池
 2: 正極電極
 3: 負極電極
 4: セパレータ

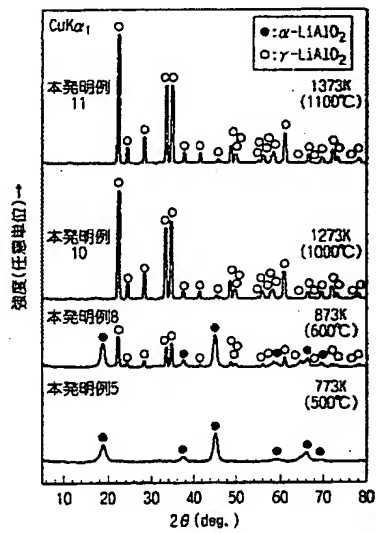
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[Figure 2]



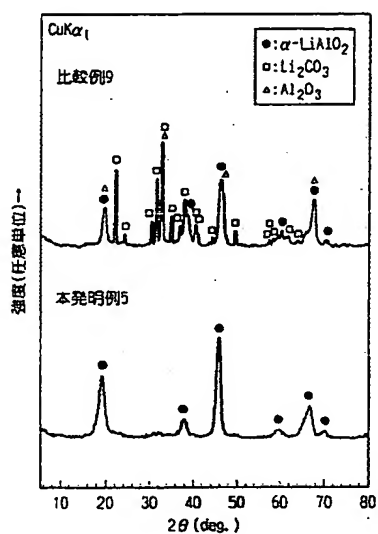
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[Figure 3]



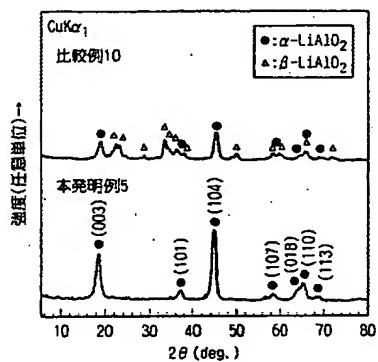
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[Figure 4]



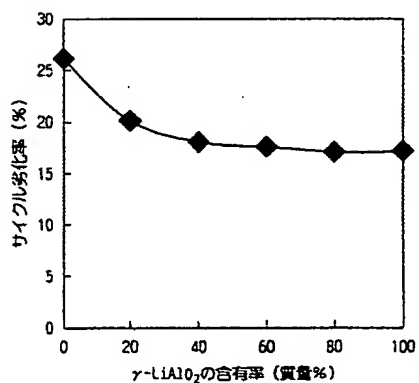
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[Figure 5]



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[Figure 6]



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